



review

OF RECENT DEVELOPMENTS

Corrosion and Compatibility

W. E. Berry • December 17, 1971

ALUMINUM ALLOYS

A comprehensive list of inhibitors and references to inhibitors for aluminum alloys has been prepared by Indian scientists.[1] Inhibitors are described for exposure to mineral acids, ammoniacal solutions, alcohols, glycols, organic bases, surface-active agents, natural atmospheres, and miscellaneous environments.

The electrochemical characteristics of aluminum galvanic anodes in the sea have been studied by the Naval Research Laboratory.[2] The experiments were conducted at Key West, Florida, on six types of commercial anode alloys. The mercury-zinc-aluminum anode consistently produced the highest efficiency with a minimum of 1250 amp hr/lb. The current capacity of indium-zinc-aluminum anodes was 757 to 900 amp hr/lb at nominal in-service current densities, while that of tin-zinc-aluminum anodes was 630 to 1000 amp hr/lb with the lowest value being obtained at low-current densities. The heat treatable tin-zinc-aluminum anodes were not considered to be suitable for galvanic anodes in seawater based on their current outputs and current capacities.

The English have studied the effect of frequency on the fatigue behavior of an age-hardening aluminum alloy in air and water environments.[3] The alloy composition was 2.5 copper, 1.5 magnesium, 1.0 iron, 1.2 nickel, and 0.1 titanium. Its tensile strength was 28.4 tonf/in² (439 MN/m²). Tests were conducted at 96 Hz and 20 kHz on cylindrical axial push/pull specimens. Shorter fatigue life was observed in water than in air. Specimens failed after a greater number of cycles at the high frequency but exhibited a decrease in real time to failure except for low stress at high frequency where the fatigue limit was apparently raised. Multiple cracking was found in the high-frequency tests in a water environment and in anodized specimens.

The influence of anodizing on the fatigue life of polycrystalline 1100 and high-purity single-crystal aluminum has been studied at Midwest Research Institute.[4] Anodized film thicknesses were 200 to 1500 Å. The fatigue life was greater in vacuum than in high humidity environments. Fatigue in vacuum produced oxide cracks that were wider and fewer in number. The mode of fracture of both oxide and matrix was strongly dependent on oxide thickness, but neither the cycles to crack initiation nor the total fatigue lives were dependent on oxide thickness.

IRON-BASE ALLOYS

Steels

The compatibility of T-1, HY-140, HP-9-4-20, and 18 Ni (200) maraging steels with N₂O₄ oxidizer and UDMH (unsymmetrical dimethyl hydrazine) has been investigated by the Aerospace Corporation.[5] Weight-loss measurements showed that the corrosion rates of the four steels in N₂O₄ were 10 to 20 times greater than for an annealed Type 304 stainless steel control sample. The 18 Ni maraging steel was pitted and the HY-140 steel exhibited crevice corrosion in N₂O₄. All four steels exhibited pitting in UDMH. No crack growth was observed in N₂O₄ or UDMH to temperatures of 120 F in precracked double-cantilever-beam specimens of the four steels. The weld metal in these four steels was also resistant to crack propagation.

The corrosion behavior of 18 Ni (180) and 18 Ni (200) maraging steels in seawater has been studied by International Nickel.[6] General corrosion rates were about half those of 4340 and HY-80 steels. Unprotected U-bends of 18 Ni (180) welds did not crack in exposures lasting one year. Similar tests with 18 Ni (180) welds produced stress-corrosion cracking after two months' exposure. Annealing these welds at 1500 F before aging or the application of cathodic protection at the potential of zinc increased the life of the U-bends. At more negative potentials, the specimens cracked readily presumably by hydrogen embrittlement. The K_{ISCC} values in seawater were 130 and 94 ksi/in^{1/2} for the Ni 18 (180) and Ni 18 (200) alloys, respectively.

The stress-corrosion-cracking behavior of 18 Ni (250) maraging steel has been studied by Syrett at the Canadian Department of Energy, Mines, and Resources.[7] Precracked specimens were exposed to 3.5 percent NaCl solution. Metallographic and fractographic examinations showed distinct differences between specimens broken under freely corroding and hydrogen-charging conditions. Syrett proposed that stress-corrosion cracking occurs by anodic path dissolution at potentials more positive than -600 mV (SCE), that hydrogen cracking occurs at potentials more negative than -800 mV, and that a mixture of the two processes occurs at -600 to -800 mV. The freely corroding maraging steel cracked at about -580 mV, presumably by anodic path dissolution.

Stainless Steels

The results of the Welding Research Council tests on the intergranular corrosion of stainless

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steels have been summarized by Crucible Steel.[8] The article lists, in tabular form, numerous environments that do or do not cause intergranular attack. In general, welding was less apt to cause intergranular attack than thermal treatment at 1100 to 1250 F, and carbon content was the most critical factor influencing sensitization susceptibility in nonstabilized stainless steels.

The Japanese claim to have developed a stress-corrosion resistant stainless steel based on studies of the effect of phosphorus and nitrogen contents in 18Cr-10Ni stainless steel on its susceptibility to stress-corrosion cracking.[9] U-bend specimens were exposed to boiling $MgCl_2$ at 154 C (309 F). The detrimental effects of phosphorus and nitrogen were less pronounced as the nickel content of the alloy was decreased. The detrimental effect of phosphorus was less pronounced as the nitrogen content decreased and vice versa. The 18Cr-10Ni alloy containing less than 0.003 weight percent phosphorus did not exhibit stress-corrosion cracking after 1000 hours' exposure even with up to 0.08 weight percent nitrogen in the alloy.

The stress-corrosion cracking behavior of cold worked A-286 has been studied at the George C. Marshall Space Flight Center.[10] C-ring (transverse) and tensile (longitudinal) specimens were exposed to the 3.5 percent NaCl alternate immersion test. No stress-corrosion cracks were detected in specimens cold worked to 53 percent reduction and exposed 180 days to the NaCl solution.

NICKEL AND COBALT ALLOYS

The effect of 1 to 8 percent aluminum additions on the oxidation of cobalt-nickel alloys has been studied at the Bureau of Mines.[11] The master alloys contained 0, 22, 50, 70, 91, and 100 weight percent nickel. The tests were conducted in oxygen at 0.5 atm and 1078, 1116, and 1156 C (1972, 2041, and 2113 F). The reaction rates generally followed the parabolic rate law. There was a general increase in the rate constants with aluminum additions up through 4 weight percent. The lowest oxidation rates were observed with the 8 weight percent aluminum additions, while the highest rates were encountered with the high-cobalt low-aluminum compositions. The following empirical relation was derived for the effect of the variables:

$$\ln(K_p) = 3.863 - 33.9 \text{ Ni/T} + 0.55 \ln [\text{Ni} \cdot (\text{Al} + 0.00001)] - 4.9 \cdot 10^6 / T^2.$$

The hot corrosion of TD Nickel and TD Nickel-Chromium has been studied at the NASA Lewis Research Center.[12] Specimens were exposed in a mach 0.5 gas stream of Jet A-1 fuel combustion products containing 2 ppm synthetic sea salt. Tests consisted of up to 500 one-hour cycles between room temperature and specimen hot-zone temperatures of 1650, 1800, and 2100 F. Hot corrosion was observed for both materials in the tests at 1650 and 1800 F. There was no evidence of hot corrosion at 2100 F, but both alloys suffered excessive metal loss. (The TD Nickel-Chromium specimen lost 4 mils per side in 200 hours' exposure).

Hypervelocity oxidation tests of TD Nickel-Chromium alloys are being conducted at the Moffett Field Ames Research Center for possible use as a reusable heat shield on the Space Shuttle Vehicle.[13] Tests were conducted at 1800 to 2200 F with a nominal

surface pressure of 15 torr. The TD Nickel-Chromium alloy lost weight steadily with time in the hypervelocity environment. The alloy experienced internal depletion of chromium and porosity. A modified alloy containing aluminum and yttrium had superior oxidation resistance, but its emissivity was considerably lower.

Three cladding compositions on IN-100 have been evaluated in thermal cycling tests conducted at the NASA Lewis Research Center.[14] The three claddings were foils of Ni-20Cr-4Al-1.2Si, Fe-25Cr-4Al-1Y, and Ni-30Cr-1.4Si alloys ranging from 0.051 to 0.254 mm in thickness. Total exposure times were up to 400 hours in 1- and 20-hour cycles to 1040 or 1090 C (1905 or 1995 F). The Ni-20Cr-4Al-1.2Si alloy cladding was the most protective, and its performance was comparable with that of a widely used commercial aluminide coating. The oxidation behavior of the Ni-Cr-Al-Si cladding was insensitive to temperature, cycle frequency, or cladding thickness. The Ni-30Cr-1.4Si alloy cladding was least protective. The oxidation resistance of all three claddings was degraded to various degrees by interdiffusion with the base metal.

The University of California at Los Angeles has studied the embrittling effects of oxygen on Rene 41, a nickel-base alloy hardened by the precipitation of gamma prime.[15] In short-time tensile tests in air at 750 to 900 C (1380 to 1650 F), oxygen promoted the initiation and propagation of intergranular cracks, while in the absence of oxygen, tensile fractures were transgranular and ductility was much improved. The sensitivity to embrittlement decreased with coarsening of the gamma prime. This effect was related to the prevention of planar pile ups of dislocations by the coarse gamma prime during plastic deformation. The pile ups were believed to be responsible for the oxygen embrittlement. The sensitivity of Rene 41 to oxygen embrittlement decreased above 900 C because general yielding is possible and the planar motion of dislocations is inhibited by coarsening of gamma prime.

The effects of applied electric fields on the oxidation of nickel and Ni-20Cr alloy in propane/air flames has been studied at Arthur D. Little.[16] A superimposed negative voltage (cathodic potential) drastically accelerated scaling reactions and sometimes altered scale morphology leading to deep penetration of corrosion products. A positive voltage (anodic polarization) decreased the reaction rate from that observed at the open-circuit potential.

TITANIUM ALLOYS

The galvanically-induced hydriding of titanium in hot salt solution has been investigated at Battelle-Northwest.[17] Galvanic couples with commercially pure and Ti-2Ni alloys were exposed to air-sparged or argon-sparged 3.4 weight percent NaCl solution at 140, 265, and 390 F. The commercially pure titanium was immune to hydriding except when coupled with aluminum. However, the Ti-2Ni alloy absorbed considerable hydrogen when coupled with aluminum and mild steel and, in some cases, when coupled with copper, nickel, and stainless steel or as an uncoupled control. Passivation of the Ti-2Ni surface by an oxide coat prior to coupling to aluminum prevented hydriding in a single test conducted at 265 F. Hydrogen pickup in the Ti-2Ni alloy was greater in the argon-sparged (oxygen poor) solutions.

Studies on the stress-corrosion cracking of titanium alloys are being continued at the Ohio State University.[18] Activation energies of 6 or 7 kcal for stress-corrosion cracking were determined for unalloyed titanium and Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-11.5Mo-6Zr-4.5Sn alloys in $\text{CH}_3\text{OH} + \text{HCl} + \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} + \text{Br}_2$ solutions suggesting that either chloride ion or titanium hydride formation describe the cracking mechanism. Studies on the effect of grain size of Ti-6Al-4V alloy on stress-corrosion cracking in $\text{CH}_3\text{OH} + \text{NaCl} + \text{H}_2\text{O}$ solution showed that increased resistance with decreasing grain size was due primarily to increased crack nucleation time.

The film growth on titanium-aluminum alloys in 3.5 percent NaCl has been measured by ellipsometry and correlated with the velocity of stress-corrosion cracking as a function of pH and applied potential in studies conducted at the Martin Marietta Research Institute for Advanced Studies.[19] The factors that stimulated film growth, such as high pH and applied anodic potentials, reduced the velocity of cracking, while those that restricted film growth, such as increasing the aluminum content of the alloy or the presence of Ti₃Al in the structure, increased the cracking velocity. As an example of these effects, the velocity of cracking in Ti-8Al-1Mo-1V alloy ranged from 0.070 cm/sec at pH 0 to about 0.009 cm/sec at pH 12.7.

MISCELLANEOUS

Compatibility tests in sulfur hexafluoride (SF_6) have been conducted at the Langley Research Center.[20] Specimens of 2024-T6 and 6061-T6 aluminum, cold rolled 1020 and 4130 steels, and annealed Type 304 and 316 stainless steels, were exposed 8, 16, and 24 hours to SF_6 at 227 C (441 F). The SF_6 did not degrade the tensile strengths of any of the materials tested.

The results of coupon corrosion studies on a number of alloys under desalination conditions have been reported by the Dow Chemical Company.[21] The corrosion performance of copper-bearing steel (ASTM A-242) was about 30 percent better than that of mild steel. Both of these steels performed well with 5 ppb oxygen in the seawater, but had high corrosion rates with greater than 100 ppb oxygen in the water. Steels containing 4 to 8 percent nickel and 3.5 percent chromium also exhibited high corrosion rates in hot water containing 125 ppb oxygen, but were not tested at the lower oxygen levels. The pitting and crevice corrosion behavior of wrought stainless steels were not consistent; preliminary ratings of stainless steel types in descending order of merit were: 316, 304, 409, and 430. Cast stainless steels CF-8, CF-8M, and CA-15 showed highly localized attack with 125 ppb oxygen in the water, but had greatly improved performance with 5 ppb oxygen in the water. The optimum conditions for aluminum alloys were 50 to 100 ppb oxygen and pH 5.0 to 5.5 during the first 10 to 24 hours followed by operation at pH 6.0 with no dependence on oxygen level in the range of 5 to 125 ppb. In contrast to the other alloys studied, the aluminum alloy performance was significantly more velocity dependent at less than 5 ppb than at 30 to 125 ppb dissolved oxygen.

Protective finishes for magnesium alloys have been studied at the Naval Air Development Center.[22] The finishes were applied on QE-22A-T6

magnesium alloy and were evaluated by cyclic exposure to 5 percent NaCl salt spray and air at 400 F. MIL-M-45202B, Type II Dow 17 anodize exhibited high corrosion resistance with several topcoat systems. Less protection was provided by hot RAE alkaline treatment which was the best of the chemical surface treatments that were evaluated. All topcoats that included MIL-L-46079A (MR) baking-type epoxy surface seal were the most resistant to corrosion. Topcoats of modified silicone epoxy, MIL-P-23377 epoxy primer, or epoxy primer-polyurethane topcoat over the preferred surface treatments were effective corrosion-resistant systems for magnesium alloys. Filling with MIL-C-24176A (SHIPS) Type II aluminum epoxy cement was effective in repairing corroded areas.

The stress-corrosion cracking behavior of stainless steels and nickel-base alloys in oxygen and NaCl-contaminated steam is being studied at Oak Ridge.[23] U-bends of welded and unwelded similar and dissimilar metals were cycled for 4 weeks between 280 and 480 C (535 and 895 F) in steam with 1.5 ppm NaCl and 20 ppm oxygen contaminants. (Specimens were cycled 5 times a week and were held at 280 C for 2 hours per cycle). No cracks were observed. In the fifth week, the NaCl concentration was increased to 10 ppm and the thermal cycle was changed to three per week with a 24-hour hold at 280 C. None of the stainless steels failed. However, two specimens of Hastelloy X welded to itself failed completely. Branching intergranular cracks were found in the heat-affected zone of the base metal adjacent to the weld.

The corrosion behavior of high-strength fastener materials has been evaluated by Standard Pressed Steel.[24] The behavior in crevices, stress-corrosion cracking, hydrogen embrittlement, and the simulated service environment was compared for some but not all material combinations. The materials (and minimum tensile strengths) were: Custom 455 (220 ksi), PH13-8Mo (220ksi), PH12-9Mo (220 ksi), Inconel 718 (220 ksi), H11 (220 and 260 ksi), Multi-phase MP35N (260 ksi), and Marage-300 (260 ksi). In general, the results showed that the ferrous alloys were susceptible to crevice corrosion, the alloys were not very susceptible to stress-corrosion (bolts torqued to 75 percent of yield and exposed to 3.5 NaCl alternate immersion), hydrogen embrittlement could be a problem, and the cracking or galvanic attack when coupled to aluminum can be reduced by applying sacrificial coatings to the bolts.

An interim report on the gaseous hydrogen embrittlement of metals has been prepared by Rocketdyne-North American Rockwell.[25] Tests were conducted in 5000 psi gaseous hydrogen at room temperature and -200 F. The embrittlement of Alloy 718 at room temperature varied considerably with condition. Embrittlement appeared to correlate with a coarse-grain structure and a nearly continuous precipitate of Ni_3Cb . The weld metal and heat affected zones of Alloy 718 were more embrittled than the base metal. The tensile properties of Inconel 625 were reduced at room temperature but not at -200 F; those of AISI 321 stainless were slightly reduced at room temperature but not at -200 F; while those of Ti-5Al-2.5Sn ELI alloy were unaffected at -200 F. The room-temperature fracture toughness of these three materials was reduced by exposure to hydrogen. Fracture-toughness tests on A-286 stainless and 2219-T87 aluminum, and tensile

and fracture-toughness tests on OFHC copper showed no embrittlement from exposure to 500 psi hydrogen.

Similar results to those described above have been reported for Alloy 718, Inconel 625, A-286, and titanium alloys in studies conducted by Pratt and Whitney. [26]

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